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PATENT SPECIFICATION (11) 1 432 157

(21) Application No. 29031/73 (22) Filed 19 June 1973
(31) Convention Application No. 61113/72
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C1H 650 721 724 726 730 731 732 734 735 737 739 740 747 752 757 758 762 763 766 767 768 773 778 782 787 813

(19)

(54) GYPSUM COMPOSITION

(71) We, JAPAN SYNTHETIC RUBBER CO. LIMITED, a Corporation organized and existing under the laws of Japan, of 1, Kyobashi-1-chome,. Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a gypsum composition and, more particularly, to an improvement in water resistance and surface hardness of a gypsum composition comprising gypsum and polyvinyl alcohol (hereinafter referred to as PVA) or comprising gypsum, PVA, and a thermosetting resin.

In recent years, molded articles of gypsum, particularly gypsum board and the like, manufactured by hardening of gypsum have been in increased demand as building materials because of their superiority in flame resistance, sound absorption, heat insulation, dimensional stability, and processability. On the other hand, however, insufficient surface hardness and inferior water resistance have restricted the use of gypsum products.

Many attempts have long been made to make gypsum lighter in weight or higher in strength by addition of high molecular weight compounds of fibrous materials. It advantages and, as a result, have found that a gypsum composition having an increased strength and improved water resistance can be obtained, without losing the merits of adding PVA, by crosslinking the PVA within the gypsum with the aid of a metal compound.

Thus, the present invention consists in an aqueous slurry comprising calcined gypsum, a polyvinyl alcohol and an aqueous solution of a metal compound other than calcium sulphate, in which the metal is from Group Ib, II, IIIa, IV, Vb, VIb, VIIb or VIII of the Periodic Table of Elements.

The Periodic Table of the Elements referred to herein is that appearing in the "Handbook of Chemistry and Physics" 51st Edition, published by The Chemical Rubber Co., Ohio, U.S.A. As is conventional in this art, the term "metal" is used herein to include the metalloids, such as silicon.

We have also discovered that, by using, in addition to PVA, a thermosetting resin, such as a melamine-formaldehyde resin or urea-formaldehyde resin and crosslinking the same, together with the PVA, with the aid of the metal compound, it is possible further to improve the strength and water resistance of the moulded gypsum products, even when the thermosetting resin and the PVA are added in small amounts. In particular, an immersing

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By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the names of JAPAN SYNTHETIC RUBBER CO. LIMITED of 1, Kyobashi-1-Chome, Chuo-Ku, Tokyo, Japan and CHICHIBU CEMENT CO. LTD. of No 4-6 1-Chome, Marunouchi, Chiyoda-Ku, Tokyo, Japan, both corporations organised and existing under The Laws of Japan.

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In recent years, molded articles of gypsum, particularly gypsum board and the like, manufactured by hardening of gypsum have been in increased demand as building materials because of their superiority in flame resistance, sound absorption, heat insulation, dimensional stability, and processability. On the other hand, however, insufficient surface hardness and inferior water resistance have restricted the use of gypsum products.

Many attempts have long been made to make gypsum lighter in weight or higher in strength by addition of high molecular weight compounds of fibrous materials. It is known, for example, that, when calcined gypsum is hardened with an aqueous solution of PVA added thereto as hydrating solution, the dispersion of PVA is good and the hardened product is improved to some degree in surface hardness and in strength, owing to the good film-forming ability of PVA (French Patent No. 1,013,252). The product, however, has disadvantages in that water resistance is too low and surface hardness is still insufficient for practical use. The present inventors have made an effort to overcome such disadvantages and, as a result, have found that a gypsum composition having an increased strength and improved water resistance can be obtained, without losing the merits of adding PVA, by crosslinking the PVA within the gypsum with the aid of a metal compound.

Thus, the present invention consists in an aqueous slurry comprising calcined gypsum, a polyvinyl alcohol and an aqueous solution of a metal compound other than calcium sulphate, in which the metal is from Group Ib, II, IIIa, IV, Vb, VIb, VIIb or VIII of the Periodic Table of Elements.

The Periodic Table of the Elements referred to herein is that appearing in the "Handbook of Chemistry and Physics" 51st Edition, published by The Chemical Rubber Co., Ohio, U.S.A. As is conventional in this art, the term "metal" is used herein to include the metalloids, such as silicon.

We have also discovered that, by using, in addition to PVA, a thermosetting resin, such as a melamine-formaldehyde resin or urea-formaldehyde resin and crosslinking the same, together with the PVA, with the aid of the metal compound, it is possible further to improve the strength and water resistance of the moulded gypsum products, even when the thermosetting resin and the PVA are added in small amounts. In particular, on immersing the moulded gypsum products in water, swelling is no longer observed and the surface hardness is much improved.

The term "polyvinyl alcohol" as used herein means a polymer containing vinyl alcohol units in its molecule. Preferably, the polymer contains 50 mole %, or more of vinyl alcohol units in its molecule. The polymers thus include homopolymers, copolymers and graft copolymers. Specific examples of polyvinyl alcohols include: saponification products of polyvinyl esters, such as polyvinyl acetate,

formate and propionate, having a degree of saponification of at least 50 mole %; saponification products of copolymers of vinyl forate, acetate or vinyl propionate and a vinyl monomer copolymerizable therewith, such as acrylonitrile, acrylic acid, maleic anhydride, methyl methacrylate, 2 - hydroxyethyl acrylate or glycidyl methacrylate, having a saponification degree of at least 50 mole %; acetalized saponification products of polyvinyl acetate, formate or propionate, having a degree of saponification of at least 50 mole %, the degree of acetalization of which is up to 15 mole percent; and graft-polymers of a vinylic or conjugated diene monomer on saponification products of polyvinyl formate, acetate or propionate having a degree of saponification of at least 50 mole per cent, examples of the vinylic or conjugated diene monomers being acrylonitrile, acrylic acid, methyl methacrylate, 2 - hydroxylethyl acrylate, glycidyl methacrylate and chloroprene, and the amount thereof being up to 5 moles per mole of the vinyl alcohol unit in the saponification product. The above-mentioned polymers may be used alone or in admixture of two or more.

The term "vinylic monomer" as used herein is defined to mean a polymerizable monomer upon the degree of polymerization and the containing ethylenic unsaturation.

The amount of PVA may vary depending upon the degree of polymerization and the degree of saponification thereof, and is usually from 0.1 to 50 parts by weight, preferably 0.5 to 20 parts by weight, per 100 parts by weight of calcined gypsum.

Suitable thermosetting resins are condensation products of melamine and formaldehyde, those of urea and formaldehyde, those of phenol and formaldehyde, those of a guanamine and formaldehyde, and derivatives of these condensation products. These resins may be used alone or in admixture of two or more. A wide range of these resins from prepolymers (i.e. simple addition products of one molecule of formaldehyde with one molecule of the other reactant to reticular polymers are used. The prepolymers are generally employed in the form of an aqueous solution, and the reticular polymers in the form of a suspension or emulsion. Although the amount of thermosetting resin used may be varied freely in accordance with the properties of the intended gypsum composition, it is generally from 0.1 to 50 parts by weight per 100 parts by weight of calcined gypsum.

The metal compounds for use in this invention which easily form a chelate bond with the hydroxyl group in the PVA, may be used alone or in admixture of two or more, and are compounds of metals of Groups Ib, II, IIIa, IV, Vb, VIb, VIIb, and VIII of the Periodic Table. Examples of the metals for use are Cu, Ag, and Au from Group Ib; Be, Mg, Ca, Sr, Ba, Zn, Cd, and Hg from Group II; Al from Group IIIa; Si, Sn, Pb, Ti, and Zr from Group IV; V and Nb from Group Vb; Cr, Mo, and W from Group VIb; Mn from Group VIIb; and Fe, Co, and Ni from Group VIII. Among these metals, Cu, Ca, Zn, Al, Si, Sn, Ti, Cr, Mo, Mn, Fe, Ni, Mg, V and Zr are preferably used in this invention. In view of pollution and color of the composition, Ca,, Si, Ti, Mg and Al are most preferable. Suitable compounds of these metals include sulfates, nitrates, carbonates, acetates, halides, hydroxides and oxides. Examples of individual compounds are copper acetate, copper nitrate, copper sulfate, copper bromide, copper iodide, magnesium iodide, calcium acetate, strontium nitrate, barium oxide, zinc chloride, zinc acetate, cadmium fluoride, mercuric acetate, aluminum chloride, aluminum sulfate, silicon dioxide, stannous chloride, stannic chloride, stannous sulfate, lead acetate, titanium sulfate, titanium hydroxide, zirconium oxychloride, vanadium trichloride, vanadium pentoxide, niobium chloride, chromous chloride, potassium bichromate, molybdenum oxide, tungstic acid, manganese chloride, manganese dioxide, manganese acetate, ferrous chloride, ferric chloride, ferric nitrate, cobaltous sulfate, cobalt acetate, nickel chloride, and nickel acetate. Calcium acetate, magnesium iodide, aluminum chloride, aluminum sulfate, silicon dioxide, and titanium sulfate are particularly preferred.

When the metal compound itself is not water-soluble, it must be made water-soluble, e.g. by the addition of an inorganic acid such as hydrogen halide, sulfuric acid, or nitric acid; an organic acid such as a carboxylic acid, for example, formic acid, or chloroacetic acid, or an organic sulfonic acid, for example, benzenesulfonic acid or *p* - toluenesulfonic acid; or an amine such as ammonia, pyridine or an alkyl derivative thereof, pyrrole or an alkyl derivative thereof, triethylenediamine, dimethylamine, or diethylamine. The above-mentioned metal compounds easily form a chelate with the hydroxyl group in the PVA, and crosslink the PVA and the thermosetting resin to cure the resins.

Acids act, in mosts cases, to adjust the start and the rate of the crosslinking reaction of PVA with a metal compound. Amines are coordinated with the metal to enhance the solubility of the metal compound in water. Therefore, the time required for crosslinking can be controlled by the quantity of an acid or amine added.

The amount of the metal compound necessary to manifest effectively the said action in the composition of this invention is within the range of 0.001 to 1 mole, preferably 0.004 to 0.1 mole per mole of hydroxy groups in PVA.

The amount of water added may be the

same as is used in producing an ordinary cast gypsum, that is, from 50 to 120 parts by weight per 100 parts by weight of calcined gypsum. The amount of PVA which can be added varies depending on the amount of water added.

A gypsum composition which has excellent strength, improved surface hardness, and resistance to penetration of water can be obtained by adding an aqueous solution of at least one compound of the metals specified (said aqueous solution may be either acidic or alkaline) together with calcined gypsum to an aqueous solution, suspension or emulsion of PVA or a mixed aqueous solution, suspension, or emulsion of PVA and a thermosetting resin, or, alternatively, adding calcined gypsum to a mixture of said liquid components, to form a viscous slurry and pouring the slurry into a desired mold to allow the slurry to solidify into a molded article. When the thermosetting resin is used, there is obtained a molded article excellent particularly in wet strength and wet hardness when immersed in water.

Polymer latexes, such as SBR latex, NBR (acrylonitrile-butadiene rubber) latex, natural rubber latex, polyvinyl acetate latex, ethylene - vinyl acetate copolymer latex, polyvinyl chloride latex, polystyrene latex, their carboxyl-containing polymer latexes, (i.e. latexes which have been modified, e.g. by emulsion copolymerization of the latex-forming monomer or monomers with a carboxyl grouu-containing monomer, to contain carboxyl groups), may be added alone or in admixture of two or more to the aqueous slurry of this invention to improve compressive strength, and nail- and wood screw-holdability. The amount thereof is preferably from 0.1 to 50 parts by weight, more preferably from 0.5 to 20 parts by weight, per 100 parts by weight of the calcined gypsum.

By adding to the aqueous slurry of this invention synthetic fibers such as rayon, Vinylon (Registered Trade Mark), nylon, and polypropylene, natural fibers or cellulose such as cotton and pulp, or mineral fibers such as glass and asbestos, it is possible to improve further the flexural strength and impact resistance of the composition and to obtain a foamed and light-weight product thereof without detracting from the merits of this invention. These fibrous materials give a maximum strength when added in an amount of from 0.5 to 10, preferably from 1 to 5, parts by weight per 100 parts by weight of calcined gypsum.

Density reduction of the gypsum composition can be effected either by foaming of PVA itself, or by addition of density-reducing materials such as foamed polystyrene beads, "Shirasu" balloon, perlite and wood flour. Addition of "Shirasu", glass powder, clay or PVA powder increases the strength of the composition. Other materials such as other filler may be added without reducing the strength of the composition. By incorporation of pigments or dyes, the gypsum composition of this invention becomes usable as decorative materials. The amount of the density-reducing material or filler added is from 0.5 to 200, preferably from 1 to 100, parts by weight per 100 parts by weight of calcined gypsum.

Shirasu is a volcanic ejecta consisting essentially of volcanic glass and having the chemical composition: SiO_2 65—73% by weight; Al_2O_3 12—18% by weight; and K_2O 5—7% by weight. The mineral content and particle size depend upon the place from which it was obtained. Shirasu balloon is a balloon obtained by melting the Shirasu and expanding the melt.

The gypsum composition of this invention may be used as a building material and a decorative material. When used in the form of a so-called gypsum board as a ceiling board or a wall board for the purposes of sound absorption and fire-proofing, the shaped articles obtained from the composition of this invention have the advantage that they need not be overlayed with paper on either side, as with conventional gypsum boards, and can be used as produced.

The invention is further illustrated below in detail with reference to Examples, but the invention should not be understood to be limited to the Examples.

In the Examples, the testing of physical properties of the gypsum composition was carried out in the following way: A test specimen was prepared by drying a solidified shaped article in an air stream at 60°C. for 48 hours, and then keeping the dried article at 20°C. and 45 to 55% relative humidity for 2 days or more. The testing for flexural strength and compressive strength was carried out according to JIS R 5201. Izod impact strength was tested on a test piece of 1.27 × 1.27 × 6.35 cm (unnotched). Following the procedure of JIS-K 5401, pencil hardness was expressed as the minimum hardness of a pencil which can scrape off the surface of the gypsum composition. The testing was conducted with pencils of 9H to 6B by use of a pencil scratch tester ("9H" shows the maximum hardness and "6B" the minimum hardness on a scale consisting of: 9H, 8H, 7H, 6H, 5H, 4H, 3H, 2H, H, F, HB, B, 2B, 3B, 4B, 5B, 6B).

Example 1.

In 600 cc of water were dissolved 10 g of a 100%-saponfied PVA having a degree of polymerization of 1,500 and 2.27 g of cupric acetate. The ratio of copper atoms to vinyl alcohol units (hereinafter expressed as Cu/OH) was 1/20. To the resulting solution was added 1,000 g of calcined gypsum and the

mixture was stirred to form a viscous slurry which was then cast to prepare a gypsum composition (this formulation is expressed as calcined gypsum : water : PVA : Cu/OH = 100 ; 60 : 1 : 1/20; similar expression shall apply hereinafter). Similarly, a number of gypsum compositions were prepared with the following combination of formulations : calcined gypsum : water : PVA : Cu/OH = 100 : 60, 80, or 100 : 1, 3, or 5 : 1/20, 1/50 or 1/100 (Table 1, Run Nos. 13 to 39). Runs Nos. 1 to 3 are Comparative Examples in which only gysum was used, and Run Nos. 4 to 12 are Comparative Examples in which only gypsum-PVA was used. The results of tests on physical properties of the above gypsum compositions were as shown in Table 1.

In Tables 2 and 3 are shown the results of tests conducted on the above gypsum compositions which had been immersed in water at 20°C. for 24 hours and then dried in an air stream at 60°C. for 48 hours, and on wet gypsum compositions after immersion in water (20°C.) for 2 hours, respectively.

From these physical characteristics, it is seen that as compared with gypsum or gypsum-PVA alone, the gypsum-PVA-metal compound systems of this invention are far superior in surface hardness and wet strength (see Tables 1, 2, and 3).

Table 1

Run No.	Formulation			Specific strength			Pencil hardness	Specific gravity (ρ = g/cm^3)
	Water (PHG)	PVA (PHG)	Cu/OH	Flexural (kg/cm^2/ρ)	Compressive (kg/cm^2/ρ)	Izod impact (kg·cm/cm^2/ρ)		
1	60	-	-	57	143	0.8	3B	1.20
2	80	-	-	40	93	1.0	Softer than 6B	0.99
3	100	-	-	25	70	0.7	Softer than 6B	0.85
4	60	1	-	84	167	1.1	HB	1.16
5	80	"	-	62	100	-	B	0.98
6	100	"	-	47	68	0.9	B	0.85
7	60	3	-	94	171	1.4	H	1.11
8	80	"	-	70	102	-	HB	0.96
9	100	"	-	58	70	1.8	HB	0.85
10	60	5	-	108	199	1.3	H	1.05
11	80	"	-	80	97	-	H	0.90
12	100	"	-	73	78	1.3	HB	0.85

Table 1 (Cont'd)

13	60	1	1/20	84	180	1.1	H	1.17
14	80	"	"	56	96	-	F	0.98
15	100	"	"	44	67	1.4	F	0.85
16	60	"	1/50	91	167	1.2	HB	1.16
17	80	1	1/50	59	91	-	B	0.97
18	100	"	"	47	69	1.1	H	0.85
19	60	"	1/100	80	153	1.0	H	1.15
20	80	"	"	52	90	-	F	0.98
21	100	"	"	40	60	1.1	HB	0.85
22	60	3	1/20	73	114	1.2	H	1.07
23	80	"	"	51	62	-	H	0.98
24	100	"	"	45	47	0.9	H	0.85
25	60	"	1/50	93	158	1.8	2H	1.09
26	80	"	"	61	86	-	3H	0.96
27	100	"	"	53	67	1.2	4H	0.85
28	60	"	1/100	98	167	1.3	4H	1.09

Table 1 (Cont'd)

29	80	3	1/100	63	100	-	4H	0.98
30	100	"	"	59	80	1.5	H	0.86
31	60	5	1/20	72	120	1.5	3H	0.99
32	80	"	"	54	70	1.2	2H	0.89
33	100	"	"	49	52	1.0	2H	0.86
34	60	"	1/50	93	137	1.5	4H	1.03
35	80	"	"	60	84	1.2	4H	0.88
36	100	"	"	58	70	0.9	4H	0.86
37	60	"	1/100	96	127	1.5	4H	1.03
38	80	"	"	63	85	1.0	3H	0.96
39	100	"	"	55	67	0.7	2H	0.85

Note: PHG denotes parts by weight per 100 parts by weight of calcined gypsum; the same shall apply hereinafter.

As is apparent from Table 1, the addition of PVA to gypsum results in an increase in strength (especially flexural strength); the addition of copper acetate does not further increase the strength but increases the surface hardness; the more PVA or copper acetate the composition contains, the higher the surface hardness becomes.

Table 2

Run No.	Formulation			Time required to reach equilibrium water content (hour)	Dry specimen *		
	Water (PHG)	PVA (PHG)	Cu/OH		Weight decrease (%)	Flexural strength (kg/cm^2)	Compressive strength (kg/cm^2)
1	60	-	-	< 1/4	1.1	73 (69)	196 (173)
4	60	1	-	1/2	1.4	84 (98)	167 (194)
7	"	3	-	3/4	1.9	90 (104)	148 (190)
10	"	5	-	1	2.2	94 (113)	156 (209)
13	60	1	1/20	1-1/2	0.8	98 (98)	191 (211)
16	"	"	1/50	2	1.0	100 (106)	215 (194)
19	"	"	1/100	4	1.1	110 (92)	162 (176)
22	"	3	1/20	24	1.0	93 (78)	142 (122)
25	"	"	1/50	24	0.9	111 (101)	168 (172)
28	"	"	1/100	24	1.1	123 (107)	188 (182)
31	"	5	1/20	> 24	1.1	68 (71)	113 (119)

Table 2 (Cont'd)

34	60	5	1/50	> 24	1.1	94 (96)	165 (141)
37	"	"	1/100	> 24	1.3	117 (99)	192 (131)
3	100	-	-	< 1/4	-	21 (21)	54 (60)
6	100	1	-	< 1/4	-	30 (38)	55 (58)
9	"	3	-	1/2	-	21 (49)	44 (59)
12	"	5	-	3/4	-	39 (62)	38 (66)
15	100	1	1/20	1/2	-	44 (37)	70 (57)
18	"	"	1/50	1	-	43 (40)	71 (59)
21	"	"	1/100	1	-	59 (34)	70 (56)
24	"	3	1/20	1	-	61 (38)	60 (40)
27	"	"	1/50	4	-	68 (45)	72 (57)
30	"	"	1/100	24	-	72 (51)	86 (68)
33	"	5	1/20	1	-	60 (42)	61 (45)
36	"	"	1/50	4	-	71 (50)	75 (60)
39	"	"	1/100	> 24	-	86 (47)	89 (57)

Note: - * After immersion in water (20°C.) for 24 hours, dried in an air stream at 60°C. for 48 hours.
Figures in parentheses are initial strengths.

From Table 2, it is seen that as compared with the case where only PVA is added, the compositions containing copper acetate in addition to PVA require far longer time to reach an equilibrium water content and most of the dry specimens show more improved strength.

Table 3

Run No.	Formulation			Wet product immersed in water (20°C) for 2 hrs.					
	Water (PHG)	PVA (PHG)	Cu/OH	Water absorption (%)	Immersed length * (mm)	Strength		Decrease in strength (%)	
						Flexural (kg/cm^2)	Compress. (kg/cm^2)	Flexural	Compress.
1	60	-	-	28	Full	37	85	56	54
4	60	1	-	29	"	27	62	77	73
7	"	3	-	31	"	24	40	82	84
10	"	5	-	21	"	27	44	80	82
13	60	1	1/20	18	"	48	81	47	47
16	"	"	1/50	10	12	51	104	45	32
19	"	"	1/100	7	1	64	113	28	22
22	"	3	1/20	9	1 - 8	47	64	40	38
25	"	"	1/50	6	2 - 3	53	87	40	35
28	"	"	1/100	4	1	69	104	29	29
31	"	5	1/20	7	6	51	64	38	34
34	60	5	1/50	4	2	62	100	29	27
37	"	"	1/100	2	1	82	126	12	5

Note:- Test specimen of the gypsum composition:
4 x 4 x 16 cm; vertically immersed in water.

From Table 3 it is seen that as compared with the case where only PVA is added, the compositions containing copper acetate in addition to PVA become more resistant to penetration of water and show only a small decrease in strength.

Example 2.

In a manner similar to that in Example 1 and using a 100% saponified PVA having a degree of polymerization of 500, gypsum compositions of the following formulation were prepared: calcined gypsum : H_2O : PVA : Cu/OH = 100 : 60 or 80 : 10 or 20 : 1/100. Physical properties were as shown in Table 4. These compositions were found to have also similar merits to those mentioned in Example 1.

Table 4

Run No.	Formulation			Specific strength			Pencil hardness	Sp. gr. (ρ =g/cm^3)
	H_2O (PHG)	PVA (PHG)	Cu/OH	Flexural (kg/cm^2/ρ)	Compress. (kg/cm^2/ρ)	Izod impact (kg.cm/cm^2/ρ)		
40	80	20	1/100	85	115	2.1	5H	0.95
41	60	10	"	100	193	1.9	5H	1.01

Example 3.

In a manner similar to that in Example 1 and using 10 types of PVA having degrees of polymerization of 500 to 2,600 and degrees of saponification of 80 to 100%, gypsum compositions of the following formulations were prepared: calcined gypsum : water : PVA : Cu/OH = 100 : 60 : 3 : 1/50. Physical properties of the compositions were as shown in Table 5. These compositions were found to have similar merits to those mentioned in Example 1.

Table 5

Run No.	PVA		Specific strength			Pencil hardness	Sp. gr. (ρ =g/cm^3)
	Degree of polymerization	Degree of saponification (%)	Flexural (kg/cm^2/ρ)	Compress. (kg/cm^2/ρ)	Izod impact (kg·cm/cm^2/ρ)		
42	2600	100	113	233	1.3	5H	1.16
43	1800	100	105	157	1.0	4H	1.15
44	1400	100	104	186	1.2	5H	1.14
45	500	100	91	168	1.5	4H	1.20
46	1700	98	94	155	1.1	3H	1.14
47	2000	88	102	172	1.0	2H	1.06
48	1700	88	92	140	1.2	2H	1.03
49	1400	88	92	142	0.8	3H	1.07
50	500	88	95	129	0.8	2H	1.14
51	1700	80	87	173	0.9	2H	1.01

From Table 5, it is seen that the greater degree of polymerization and degree of saponification of PVA, the higher the strength and surface hardness of the gypsum composition become.

Example 4.

Following the procedure of Example 1 and using PVA having a degree of polymerization of 1,500 and a degree of saponification of 100%, gypsum compositions were prepared by molding a slurry of the following formulation which had been filled with 1, 3 or 5 PHG of glass fiber, 8 mm in length and 10 μm in diameter (Run Nos. 52 to 54), Vinylon fiber, 5 mm in length and 0.25 μm in diameter (Run Nos. 55 to 57), or polypropylene fiber, 3 mm in length and 0.25 μm in diameter (Runs Nos. 58 to 60) calcined gypsum : water : PVA : CuOH = 100 : 100 : 3 : 1/50.

In a similar manner, gypsum compositions were prepared from a slurry of the same formulation which had been filled with 5, 10, 30, or 50 PHG of "Shirasu", 24 mesh (U.S. Standard) or smaller size (Run Nos. 61 to 64; Comparative Examples 65 66). Physical properties of the above compositions were as shown in Table 6. Similar merits to those mentioned in Example 1 were found.

Table 6

Run No.	Formulation					Specific strength			Sp. gr. (ρ =g/cm3)	Pencil hardness
	Water (PHG)	PVA (PHG)	Cu/OH	Filler		Flexural (kg/cm2/ρ)	Compress. (kg/cm2/ρ)	Izod impact (kg·cm/cm2/ρ)		
				Type	Amount (PHG)					
52	100	3	1/50	Glass fiber	1	57	70	3.3	0.83	4H
53	"	"	"	"	3	76	67	9.3	0.84	5H
54	"	"	"	"	5	76	> 80	17.4	0.75	5H
55	"	"	"	Vinylon fiber	1	69	81	3.0	0.83	4H
56	"	"	"	"	3	77	87	5.4	0.84	5H
57	"	"	"	"	5	80	83	9.1	0.75	5H
58	"	"	"	PP fiber	1	66	74	2.7	0.82	6H
59	"	"	"	"	3	68	78	5.5	0.81	5H
60	"	"	"	"	5	67	68	5.6	0.75	5H
61	60	"	"	Shirasu	5	84	152	0.9	1.17	4H
62	"	"	"	"	10	101	184	2.0	1.16	4H
63	"	"	"	"	30	72	134	0.9	1.00	5H
64	"	"	"	"	50	43	82	1.1	0.89	6H
65	60	-	-	Shirasu	5	50	160	-	1.21	3B
66	"	-	-	"	10	60	135	-	1.26	2B

It is seen that when filled with fibers, the composition is improved in flexural strength and impact resistance and that an effect of the addition of copper acetate is recognizable in surface hardness while the tendency of the water resistance was similar to that in Example 1.

Example 5.

a) Following the procedure in Example 1 and using PVA having a degree of polymerization of 1,500 and a degree of saponification of 100% and molybdenum oxide dissolved in 30%-aqueous ammonia, gypsum compositions of the following formulations were prepared: calcined gypsum : water : PVA : Mo/OH : 30%-aqueous ammonia = 100 : 60 or 100 : 3 or 1 : 1/100 or 1/50 : 10 (Runs Nos. 67 to 70).

b) In a similar manner and using a 35%-aqueous solution of titanium sulfate, gypsum compositions of the following formulations were prepared : calcined gypsum : water : PVA : Ti/OH = 100 : 60, 80, 100 : 1 or 3 : 1/50 (Run Nos. 71 to 75).

c) In a similar manner and using an aqueous solution of titanium sulfate admixed with concentrated hydrochloric acid, gypsum compositions of the following formulations were prepared: calcined gypsum : water : PVA : Ti/OH : concentrated hydrochloric acid = 100, : 60, 80, or 100 : 3 : 1/50 : 0.5 to 0.1 (Run Nos. 76 to 78).

d) In a similar manner and using an aqueous solution of zinc acetate admixed with triethylenediamine, gypsum compositions of the following formulations were prepared: calcined gypsum : water : PVA : Zn/OH : triethylenediamine = 100 : 60, 80 or 100 : 1 : 1/150 : 0.001 (Runs Nos. 79 to 81).

e) In a similar manner and using potassium bichromate, gypsum compositions of the following formulations were prepared: calcined gypsum : water : PVA : Cr/OH = 100 : 60 : 1 or 3 : 1/50 (Run Nos. 82 and 93).

Physical properties of the gypsum compositions a) to e) were as shown in Table 7. Effects similar to those mentioned in Example 1 were observed.

Table 7

Run No.	Formulation						Specific gravity (ρ =g/cm3)	Specific strength		Pencil hardness
	Water (PHG)	PVA (PHG)	Metal compound	M/OH	Additive	Amount of additive (PHG)		Flexural ($kg/cm^2/\rho$)	Compressive ($kg/cm^2/\rho$)	
67	60	3	MoO_3	1/100	30%-aq. ammonia	10	1.15	99	148	4H
68	"	"	"	1/50	"	"	1.11	107	176	4H
69	100	1	"	1/100	"	"	1.20	100	186	2H
70	"	"	"	1/50	"	"	1.20	108	150	3H
71	60	1	$Ti(SO_4)_2$	1/50	-	-	1.16	95	219	4H
72	80	"	"	"	-	-	1.00	77	110	3H
73	100	"	"	"	-	-	0.87	48	79	3H
74	80	3	"	"	-	-	0.95	86	115	5H
75	100	"	"	"	-	-	0.86	65	87	3H
76	60	3	"	"	conc. HCl	0.5	1.05	94	130	2H
77	80	"	"	"	"	0.1	0.89	70	94	H
78	100	"	"	"	"	0.1	0.80	59	75	H

Table 7 (Cont'd)

79	60	1	$Zn(AcO)_2$	1/150	Triethylene-diamine	0.001	1.22	98	152	3H
80	80	"	"	"	"	"	1.00	63	97	2H
81	100	"	"	"	"	"	0.87	55	77	2H
82	60	1	$K_2Cr_2O_7$	1/50	-	-	1.21	105	212	5H
83	"	3	"	"	-	-	1.17	107	201	6H

With the addition of an aqueous solution of various metal compounds, the surface hardness becomes higher and the water resistance shows a tendency similar to that mentioned in Example 1.

Example 6.

a) In 700 cc of water was dissolved 30 g of PVA having a degree of polymerization of 1,500 and a degree of saponification of 89%. The solution was mixed with 3.30 g of aluminum chloride hexahydrate (corresponding to Al/OH = 1/50) dissolved in 100 ml of 1.8 N - hydrochloric acid. To the resulting mixed solution was added 1,000 g of calcined gypsum and the mixture was stirred to form a viscous slurry which was then cast-molded and dried at 60°C for 48 hrs. to prepare a gypsum composition. (This formulation is expressed as calcined gypsum : water : PVA : Al/OH : hydrogen chloride = 100 : 80 : 3 : 1/50 : 0.65). (Run No. 84).

b) In a similar manner and using 3.1 g of stannous chloride dihydrate dissolved in 100 ml of 1 N - hydrochloric acid, a gypsum composition of the following formulation was prepared: calcined gypsum : water : PVA : Sn/OH : hydrogen chloride = 100 : 80 : 3 : 1/50 : 0.36 (Run No. 85).

c) In a similar manner and using 1.2 g of vanadium pentoxide dissolved in 100 ml of 3,6 N - hydrochloric acid, a gypsum composition was prepared with the following formulation: calcined gypsum : water : PVA : V/OH : hydrogen chloride = 100 : 80 : 3 : 1/50 : 1.3 (Run No. 86).

d) In a similar manner and using 3.7 g of ferric chloride hexahydrate dissolved in 100 ml of water, gypsum compositions were prepared with the following formulation: calcined gypsum : water : PVA : Fe/OH = 100 : 60, 80, or 100 : 1, 2, 3, 4, or 5 : 1/10, 1/20 : 1/50, 1/100, or 1/200 (Run Nos. 87 to 97).

e) In a similar manner and using 1.09 g of calcium acetate dissolved in 100 ml of 1.4%-aqueous ammonia, a gypsum composition was prepared with the following formulation: calcined gypsum : water: PVA : Ca/OH : ammonia = 100 : 3 : 1/100 : 0.03 (Run No. 98).

In Table 8 are shown the results of testing for physical properties of the gypsum compositions a) to e) which had been dried at 60°C. for 48 hours.

Table 8

Run No.	Formation						Specific gravity (ρ = g/cm^3)	Specific strength			Pencil hardness
	Water (PHG)	PVA (PHG)	Metal compound	M/OH	Additive	Amount of additive (PHG)		Flexural (kg/cm^2/ρ)	Compressive (kg/cm^2/ρ)	Izod impact strength (kg·cm/cm^2/ρ)	
84	80	3	$AlCl_3 \cdot 6H_2O$	1/50	1.8N HCl	0.65	0.95	84	71	1.0	4H
85	"	"	$SnCl_2 \cdot 2H_2O$	"	1N HCl	0.36	0.92	97	117	1.2	5H
86	"	"	V_2O_5	"	3.6N HCl	1.3	1.01	68	92	1.1	3H
87	60	3	$FeCl_3 \cdot 6H_2O$	"	-	-	1.10	98	155	1.7	5H
88	80	1	"	"	-	-	1.01	56	111	0.9	4H
89	"	2	"	"	-	-	1.01	68	77	0.9	5H
90	"	3	"	1/200	-	-	1.02	71	82	1.1	6H
91	"	"	"	1/100	-	-	0.94	73	71	1.4	5H
92	"	"	"	1/50	-	-	1.00	89	108	1.2	5H
93	"	"	"	1/20	-	-	0.98	86	95	2.5	6H
94	80	3	$FeCl_3 \cdot 6H_2O$	1/10	-	-	1.00	73	74	1.0	5H
95	"	4	"	1/50	-	-	0.99	96	103	1.1	5H
96	"	5	"	"	-	-	0.89	93	85	1.0	5H
97	100	3	"	"	-	-	0.99	81	96	1.4	5H
98	100	3	$Ca(CH_3COO)_2$	1/100	1.4%-aq. ammonia	0.03	0.86	108	115	1.2	6H

From Table 8 it is seen that with the addition of an aqueous solution of compounds of metals of Group IIa, IIIa, IVa, Vb, and VIIb the surface hardness becomes higher and the water resistance shows a tendency similar to that mentioned in Example 1.

Example 7.

In 500 ml of water were dissolved 10 g of PVA having a degree of polymerization of about 1,500 and a degree of saponification of about 86% and 5 g (solids) of a melamine-formaldehyde pre-condensation product (synthesized by suspending melamine in formalin in a ratio of 3 moles of formaldehyde per mole of melamine and heating at 80°C. for 20 minutes). To the resulting solution was added 0.454 g of cupric acetate (corresponding to Cu/OH = 1/100) and uniformly dissolved. The resulting solution was admixed with 500 g of calcined gypsum, stirred for 2 minutes by means of a mixer, poured into a mold, and allowed to harden. In Table 9 are shown properties of the hardened article which had been dried at 60°C. for 48 hours.

Example 8.

In 500 ml of water were dissolved 10 g of the PVA used in Example 7 and 5 g (solids) of a melamine - formaldehyde resin emulsion (prepared by suspending melamine in formalin in a ratio of 3 moles of formaldehyde per mole of melamine and heating at 80°C. for 1 hour). To the resulting solution were added 11 ml of a 5%-aqueous solution of titanium sulfate (corresponding to Ti/OH=1/100) and 500 g of calcined gypsum. A molded article was obtained from the mixture according to the procedure mentioned in Example 7. In Table 9 are shown properties of the molded article.

Example 9.

In 500 ml of water were dissolved 10 g of PVA and 5 g (solids) of a water-soluble urea - formaldehyde resin (synthesized from a mixture of 1 mole of urea and 1.6 mole of formaldehyde, which had been adjusted to a pH of 7 with sodium hydroxide, by heating at 100°C. for 45 minutes). To the resulting solution were added 11 ml of a 5%-aqueous solution of titanium sulfate and 500 g of calcined gypsum. A molded article was obtained from the mixture in a manner similar to that in Example 7. In Table 9 are shown properties of the molded article.

Example 10.

The same composition as in Example 7 was admixed with 15 g of glass fiber and a moulded article was obtained from the mixture. In Table 9 are shown properties of the molded article.

Example 11.

The same composition as in Example 7 was admixed with 5 g of foamed polystyrene beads and a molded article was obtained from the mixture. In Table 9 are shown properties of the molded article.

Example 12.

In a manner similar to that in Example 7, a gypsum molded article was prepared from 15 g of PVA, 0.545 g of cupric acetate, 500 g of calcined gypsum, and 500 ml of water. The test results of properties of the article were as shown in Table 9.

Referential Example 1.

In a manner similar to that in Example 7, a gypsum molded article was prepared from 10 g of PVA, 5 g of melamine-formaldehyde resin ("Sumirez Resin 613", produced by Sumitomo Chemical Co.), 500 g of calcined gypsum, and 500 ml of water. The test results of properties of the article were as shown in Table 9.

Table 9

Example No.	7	8	9	10	11	12	Ref. Ex. No. 1
Specific gravity	0.90	0.90	0.90	1.20	0.60	0.90	0.90
Compressive strength (kg/cm^2)	102	99	100	150	60	80	45
Flexural strength (kg/cm^2)	85	87	84	110	70	70	50
Surface hardness (pencil hardness)	8H	8H	8H	9H	4H	6H	3H
Water absorption after 24 hours (%)	4	6	7	3	5	50	50
Surface hardness after immersion in water at 20°C. for 1 hour	2H	2H	2H	2H	B	6B	6B
Change in appearance after immersion in water at 20°C. for 1 hour	none	none	none	none	none	Swell-up	Bleeding of PVA

Example 13.

The same procedure as in Example 1 was repeated using 100 g of calcined gypsum, 3 g of 99.4% saponified PVA having a degree of polymerization of 1,500, cupric acetate (Cu/OH =1/100), 2 g (solids) of carboxylated SBR latex (methacrylic acid/styrene/butadiene = 5/25/70 by weight) to obtain a gypsum composition. The results of tests on physical properties of the gypsum composition were as shown in Table 10.

Example 14.

The same procedure as in Example 7 was repeated, except that an emulsion of a graft polymer of methyl methacrylate on 99.4%-

saponified PVA having a degree of polymerization of 1,500 (the vinyl alcohol/ methyl methacrylate molar ratio being 1) was substituted for the PVA, and $SnCl_2$ was substituted for the cupric acetate to obtain a gypsum composition. The results of tests on physical properties thereof were as shown in Table 10.

Example 15.

The same procedure as in Example 7 was repeated, except that 99.4%-saponified PVA having a degree of polymerization of 1,500 was substituted for the PVA, $AlCl_3$ (corresponding to Al/OH = 1/200) was substituted for the cupric acetate and 1 g (solids) of an NBR latex (acrylonitrile/butadiene = 35/36 by weight) was used together to obtain a gypsum composition.

The results of tests on physical properties were as shown in Table 10.

Table 10

Example No.	Specific gravity	Compressive strength (kg/cm^2)	Flexural strength (kg/cm^2)	Surface hardness (pencil)	Water absorption (%)	Surface hardness after immersion*
13	0.85	108	85	5H	35	3B
14	0.92	120	91	8H	6	2H
15	0.88	123	88	6H	4	2H

Note: * In water at 20°C for 1 hr.

In Examples 13 and 15, it was found that the nail- and wood screw-holdability was improved.

WHAT WE CLAIM IS:—

1. An aqueous slurry comprising calcined gypsum, a polyvinyl alcohol and an aqueous solution of a metal compound other than calcium sulphate, in which the metal is from Group Ib, II, IIIa, IV, Vb, VIb, VIIb or VIII of the Periodic Table of the Elements.

2. An aqueous slurry according to claim 1, in which the amount of water in said aqueous slurry is from 50 to 120 parts by weight per 100 parts by weight of said calcined gypsum.

3. An aqueous slurry according to claim 1 or claim 2, in which said metal is copper, zinc, tin, chromium, molybdenum, manganese, iron, nickel, vanadium or zirconium.

4. An aqueous slurry according to claim 1 or claim 2, in which said metal is calcium, silicon, titanium, magnesium or aluminium.

5. An aqueous slurry according to claim 1 or claim 2, in which said metal compound is a sulphate, a nitrate, a carbonate, an acetate, a halide, a hydroxide or an oxide.

6. An aqueous slurry according to any one of the preceding claims, additionally comprising an acid or an amine.

7. An aqueous slurry according to claim 6, in which said amine is ammonia, pyridine, pyrrole, triethylenediamine, dimethylamine or diethylamine.

8. An aqueous slurry according to any one of the preceding claims, additionally comprising from 0.5 to 200 parts by weight per 100 parts by weight of said calcined gypsum of a filler.

9. An aqueous slurry according to any one of the preceding claims, in which the amount of said metal compound is from 0.001 to 1 mole per mole of hydroxyl groups of said polyvinyl alcohol.

10. An aqueous slurry according to claim 9, in which the amount of said metal compound is from 0.004 to 0.1 mole per mole of hydroxyl groups of said polyvinyl alcohol.

11. An aqueous slurry according to any one of the preceding claims, additionally containing a synthetic fibre, a natural fibre, cellulose or an inorganic fibre.

12. An aqueous slurry according to claim 11, in which the amount of said fibre is from 0.5 to 10 parts by weight per 100 parts by weight of said calcined gypsum.

13. An aqueous slurry according to any one of the preceding claims, in which the amount of polyvinyl alcohol is from 0.1 to 50 parts by weight per 100 parts by weight of said calcined gypsum.

14. An aqueous slurry according to any one of the preceding claims, additionally comprising a thermosetting resin.

15. An aqueous slurry according to claim 14, in which the amount of said thermosetting resin is from 0.1 to 50 parts by weight per 100 parts by weight of said calcined gypsum.

16. An aqueous slurry according to claim 14 or 15, in which said thermosetting resin is a condensation product of melamine and formaldehyde, a condensation product of a urea and formaldehyde, a condensation product of a phenol and formaldehyde, a condensation product of a guanamine and formaldehyde, or a derivative thereof.

17. An aqueous slurry according to any one of the preceding claims, in which said metal compound is copper acetate, copper nitrate, copper sulfate, copper bromide, copper iodide, strontium nitrate, barium oxide, zinc acetate, zinc chloride, cadmium fluoride, mercuric acetate, stannous chloride, stannic chloride, stannous sulfate, lead acetate, titanium hydroxide, zirconium oxychloride, vanadium trichloride, vanadium pentoxide, niobium chloride, chromous chloride, potassium dichromate, molybdenum oxide, tungstic acid, manganese chloride, manganese dioxide, manganese acetate, ferrous chloride, ferric chloride, ferric nitrate, cobaltous sulfate, cobalt acetate, nickel chloride, or nickel acetate.

18. An aqueous slurry according to any one of claims 1 to 16, in which said metal compound is calcium acetate, silicon dioxide, titanium sulfate, aluminum chloride, aluminum sulfate or magnesium iodide.

19. An aqueous slurry according to any one of the preceding claims, in which said polyvinyl alcohol is: a saponification product of polyvinyl formate, polyvinyl acetate or polyvinyl propionate; a saponification product of a copolymer of vinyl formate, vinyl acetate or vinyl propionate and a vinylic monomer copolymerizable therewith; an acetalized saponification product of polyvinyl formate, polyvinyl acetate or polyvinyl propionate, the degree of acetalization being up to 15 mol %; or a graft copolymer of a vinylic or conjugated diene monomer on a saponification product of polyvinyl formate, polyvinyl acetate or polyvinyl propionate, the proportion of said vinylic or conjugated diene monomer being up to 5 moles per 1 vinyl alcohol unit in the saponification product; or a mixture of two or more thereof, said saponification products having a degree of saponification of at least 50 mol %.

20. An aqueous slurry according to claim 19, in which said copolymer is a copolymer of vinyl formate, vinyl acetate or vinyl propionate with acrylonitrile, acrylic acid, maleic anhydride, methyl methacrylate, 2-hydroxyethyl acrylate or glycidyl methacrylate.

21. An aqueous slurry according to claim 18, in which said graft copolymer is of acrylonitrile, acrylic acid, methyl methacryl-

ate, 2 - hydroxyethyl acrylate, glycidyl methacrylate or chloroprene on the saponification product of polyvinyl formate, polyvinyl acetate or polyvinyl propionate.

22. An aqueous slurry according to claim 6, in which said acid is a hydrogen halide, sulphuric acid, nitric acid, formic acid, chloroacetic acid, benzenesulphonic acid or *p*-toluene - sulphonic acid.

23. An aqueous slurry according to any one of the preceding claims, additionally comprising from 0.5 to 200 parts by weight, per 100 parts by weight of said calcined gypsum, of foamed polystyrene beads, "Shirasu" balloon, perlite, or wood flour.

24. An aqueous slurry according to claim 8, in which said filler is "Shirasu", powdered glass, clay or powdered polyvinyl alcohol.

25. An aqueous slurry according to any one of the preceding claims, additionally comprising from 0.1 to 50 parts by weight per 100 parts by weight of said calcined gypsum, of an SBR latex, NBR latex, natural rubber latex, polyvinyl acetate latex, ethylenevinyl acetate copolymer latex, polyvinyl chloride latex, polystyrene latex or their carboxyl-containing polymer latices.

26. An aqueous slurry according to claim 1, substantially as hereinbefore described with reference to the foregoing Examples.

27. A process for the production of a gypsum composition by hardening an aqueous slurry according to any one of the preceding claims.

28. A process according to claim 27, in which said slurry is moulded prior to hardening.

29. A gypsum composition when produced by a process according to claim 27 or claim 28.

30. The use of a gypsum composition according to claim 29 as a building material.

MARKS & CLERK,
Chartered Patent Agents,
57—60, Lincoln's Inn Fields,
London, WC2A 3LS.
Agents for the Applicants.

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